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Removal of ametryn through nanofiltration and reverse osmosis

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ABSTRACT

This study focused on the performance of nanofiltration (NF) and reverse osmosis (RO) in the removal of ametryn. Here, we investigated the effects of the applied pressure and ionic conditions on the removal of ametryn from water. It was found that the adsorption of ametryn onto NF membrane to decrease with the increase in ionic strength. Increased interaction between the NaCl electrolyte and the membrane surface is considered as the reason for the reduction in the adsorption. However, adsorption of ametryn onto the RO membrane did not show any trend. The removal of ametryn by NF and RO found to increase with the increase in the ionic strength. Retention of electrolyte salt (NaCl) on the membrane surface tends to decrease the membrane pore size which in turn increases the removal of ametryn at higher ionic strengths. It was found that up to 92% of ametryn could be removed using RO.

Keywords: Adsorption; Ametryn; Ionic strength; Nanofiltration; Rejection; Reverse osmosis

1. Introduction

Water is a vital part of everyday life. It is essential that humans have an adequate supply of clean water to avoid illness and disease. It is for this reason that water pollution is one of the main challenges that mankind must face. Although water pollution remains an overwhelming problem in developing nations, industrialised nations, such as Australia, still have to contend with the reality of contaminated waterways. Ametryn is an herbicide that is commonly used to control broadleaf and grass weeds in crops such as corn, pineapple and sugar cane [1–3]. Although it is considered to be low to slightly toxic in humans, it could pose a threat if consumed in high enough doses [3]. It is considered to be highly toxic to aquatic life such as crustaceans and molluscs [1]. Research has shown that ametryn can be found in high concentrations in rivers and waterway that eventually flow into the sea. One particular study found that ametryn was present in rivers and streams flowing into the Great Barrier Reef due to their proximity to sugar cane plantations [4] and around 0.30 μg/L of ametryn was found in Queensland [5]. The impact of ametryn on the pristine ecosystem of the Great Barrier Reef is potentially damaging.

A study by Wang et al. [6] focused on one particular pesticide, diuron, and the influence of ionic conditions and operating pressures on the rejection rate through a nanofiltration membrane. The study found that better rejection rates could be achieved

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with intermediate ionic strength (0–0.02 M) and a lower operating pressure (at 5 bar as opposed to 25 bar). The study also found that a larger ionic strength had a shielding effect on the adsorption of diuron, with the effect much greater at 5 bar than at 25 bar.

Another study was conducted by Boussahel et al. [7] on the effects of the presence of organic and inorganic matter on the removal of a number of pesticides using NF membranes. It was found that the presence of organic matter (humic acid) and inorganic matter (sulphates and chlorides) helped to improve the rejection of the pesticides through the NF membranes (with the exception of diuron). This occurred due to either macromolecules formed with the pesticide molecules or by similarly reducing the pore size of the membranes.

A study conducted by Lipp et al. [8] in the removal of organic micro-pollutants using RO and NF membranes found that the molecular weight of the pollutant had an impact on compound rejection with a larger molecular weight resulting in greater rejection. The study also found that the RO membranes performed better than their NF equivalents in removing the pollutants.

Another study by Wang et al. [9] investigated the influence that coagulation has on the removal of lower molecular weight organic compounds by nanofiltration. The study found that coagulation improved compound removal but increased membrane fouling. The study also found the addition of NaCl rather than polyaluminium chloride resulted in better removal with no further fouling of the membrane.

Ametryn can be classified as a lower molecular weight persistent organic pollutant (LMWPOP) due to its small molecular weight (<1,000 Da) and its inability to decay rapidly in the natural environment. Due to its longevity in the environment and its impact on aquatic life, it is undesirable for ametryn to be present in waterways. There is a vital need to remove LMW-POPs, such as ametryn, from waterways to ensure the wellbeing of aquatic life. This study evaluates efficiencies of nanofiltration (NF) and reverse osmosis (RO) in removing ametryn from water.

2. Theoretical model of rejection and pore sizes

It is often useful to know what the rejection of a certain compound will be through a membrane filter without conducting practical experiments. Research carried out by Kiso et al. [10] provided a method of determining the theoretical removal of pesticides through a given pore size or vice versa. A method

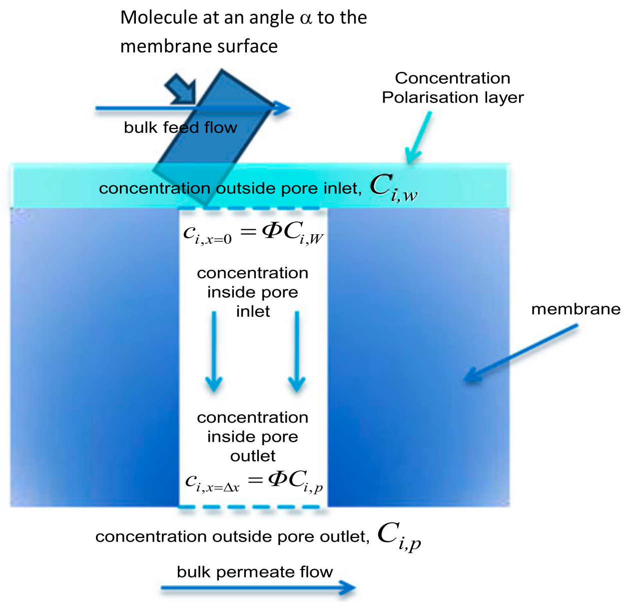


Fig. 1. passage of a molecule through a pore of a membrane at a time step, *i*.

used to determine the theoretical rejection when the pore size of a membrane is known is outlined below.

To determine the theoretical solute rejection, R_i, a number of factors must be known. The pore size of the membrane (r_p), the applied pressure (ΔP) and the dimensions of the molecule are required (Fig. 1). The dimensions of the molecule refer to the maximum length of the molecule (L) (distance from the two outer most atoms plus the atoms' Van der Walls radius) and the width (MWd) perpendicular to the maximum length. Using this information, the theoretical solute rejection can be found through the model developed by Kiso et al. [10]. The dimensions of the molecule can be determined using MOPAC software [10]. In order to estimate the pore size of a membrane, the theoretical rejection values R_i obtained for different flux values J_v have to be matched with the corresponding experimental rejection values by adjusting the pore size of the membrane.

3. Materials and methods

3.1. Materials

The experiments were conducted using a laboratory-scale filtration unit (RNF-0460) attached to a 15-L feed tank cooled by a heat exchange jacket. A representation of this unit can be seen in Fig. 2.

The membranes used in the experiments were a spiral wound RO membrane (SG1812C-28D) and a spiral wound NF membrane (DK1812C-34D) both

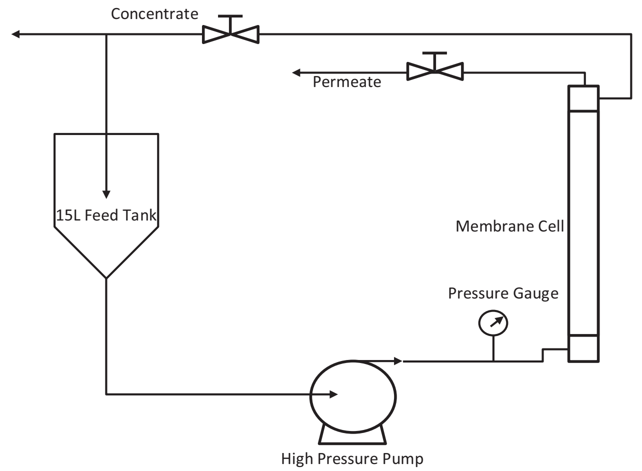


Fig. 2. Laboratory scale filtration unit used to conduct NF and RO experiments.

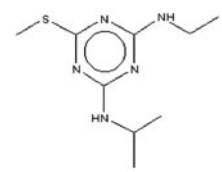
Table 1
Membrane properties

Property	SG 1812C-47P (RO)	DK 1812C-34D (NF)
Active area (m^2)	0.27	0.32
NaCl rejection (%)	97	–
$MgSO_4$ rejection (%)	–	98
pH range	3–10	3–9
Maximum pressure (kPa)	4,137	4,137
Molecular weight cut-off (Da)	–	200

manufactured by the General Electric Company. The characteristics for each membrane are shown in Table 1. The above NF membrane was used as it had a molecular weight cut-off that is similar to the molecular weight of ametryn, and RO membrane was selected to compare the performance of the NF membrane.

In these experiments, it would have been impractical to use natural samples of water as the concentration of ametryn would have been difficult to ascertain and the samples would have contained many other pollutants irrelevant to this study. Preparing the samples in a laboratory allowed for precise concentrations. Due to the low solubility of ametryn in water, it was first necessary to dissolve the compound in methanol. The solution was then heated in a rotary evaporator to allow the methanol to dissolve. For this study, samples of water were dosed at approximately 1 mg/L. The properties of ametryn can be seen in Table 2. To replicate the effects of an ionic environment, sodium chloride was added to the solution to maintain the ionic conditions.

Table 2
Physical and chemical properties of ametryn

Physical/chemical property	Description/magnitude
Chemical structure	
IUPAC name	N2-ethyl-N4-isopropyl-6-methylthio-1,3,5-triazine-2,4-diamine
Appearance	White powder
Chemical formula	$C_9H_{17}N_5S$
Molecular weight (g/mole)	227.33
Molecular length (Å)	12.5
Molecular width (Å)	6.1
Solubility in water (ppm)	185 (at 20˚C) and readily dissolves in solvents (acetone)
Purpose	To control grass

3.2. Adsorption and filtration

Numerous experiments were conducted under varying conditions. The concentration of the compound remained constant throughout the experiments at 1 mg/L, as did the flow rate at 8 L/min. Other factors differed throughout the experiments: ionic strengths of 0, 0.001, 0.01 and 0.1 M; and operating pressures of 25 and 35 bar in the RO membrane, and 5, 7.5 and 10 bar in the NF membrane. Larger pressures in RO were chosen to obtain higher fluxes.

Initially, the filtered permeate was allowed to recirculated through the system for a period of 6 h in order to allow for the maximum adsorption of the compound to occur on the membrane surface. Six hours were chosen after which there was no significant change in the concentration of ametryn in the permeate was observed. Samples were taken throughout this time to determine the levels of adsorption. After this period of adsorption, the permeate output was removed from the feed tank and collected above a set of electronic scales. The weight was recorded to determine the flux of the permeate. Samples of the permeate, concentrate and feed were taken at regular intervals until the majority of the solution had passed through the membrane. The samples were later used to determine the extent of ametryn removal by the membrane. Single runs were conducted for all experimental conditions. However, due care was taken to obtain accurate data for all experiments. The flux results obtained under each experimental condition were in agreement with previous experiments conducted using the same membrane unit [9].

3.3. Analysis of samples

To determine the amount of ametryn remaining in the water, a Merck spectrometer was used. The absorbance measurements were taken with a UV wavelength of 222 nm and compared against a standard curve of known concentrations to determine the level of compound remaining in each sample. The pH of the samples was regularly tested throughout the experiments using a WTW 315i pH Meter, as was the temperature (Hanna Instruments Minitherm HI8751 digital thermometer), the conductivity (WTW LF330 conductivity meter) and the turbidity (Hach 2100P Turbidimeter).

3.4. Flux

Flux was an important parameter to measure as it could indicate fouling within the membrane. During the filtration stage, the mass of permeate that had passed through the membrane was measured at regular intervals. The flux was then determined using the following equation:

$$J_i = \frac{m_i - m_{i-1}}{\rho A(t_i - t_{i-1})} \tag{1}$$

where J_i = flux at interval i (L/m^2 h); m_i = mass of sample at t_i (kg); ρ = density of solution (kg/m^3); A = area of membrane cross section (m^2); t_i = time from the beginning of filtration to the end of interval i (h).

The average flux for each experiment was calculated using the following equation [6]:

$$J = \frac{\sum_{i=1}^{t_n} J_i}{t_n} \tag{2}$$

where J = average flux (L/m^2 h); t_n = the number of time intervals during which the flux data were collected.

A density of a 1,000 kg/m^3 was used for the water.

4. Results and discussion

4.1. Adsorption of ametryn by NF and RO membranes

The adsorption results were obtained from the first 6 h of each experiment, during which the permeate was recirculated through the system. Adsorption is an indication of the level of compound adsorption the membrane can achieve, that is, removing a percentage of the compound from the recirculating solution. It was assumed that after 6 h all possible adsorption had occurred [6].

It can be seen in Fig. 3 that the presence of sodium chloride generally inhibited ametryn adsorption by the membrane. In Fig. 3, 0 M NaCl denotes ametryn solution without any salt. Electrostatic interaction between the membrane and the electrolyte NaCl will increase with the increase in the concentration of NaCl. This could lead to the reduction in adsorption of ametryn by the membrane surface, with the increase in the concentration of NaCl. Similar trend was observed when diuron was used as the model solute [9]. Although adsorption of diuron showed

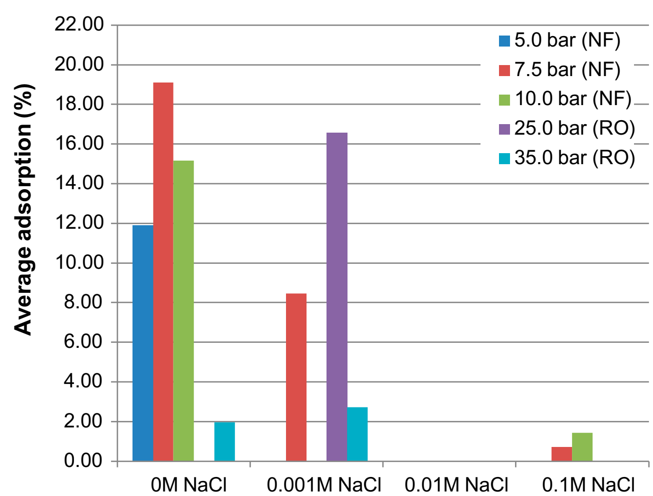


Fig. 3. Average adsorption of ametryn by NF and RO membranes at different ionic conditions.

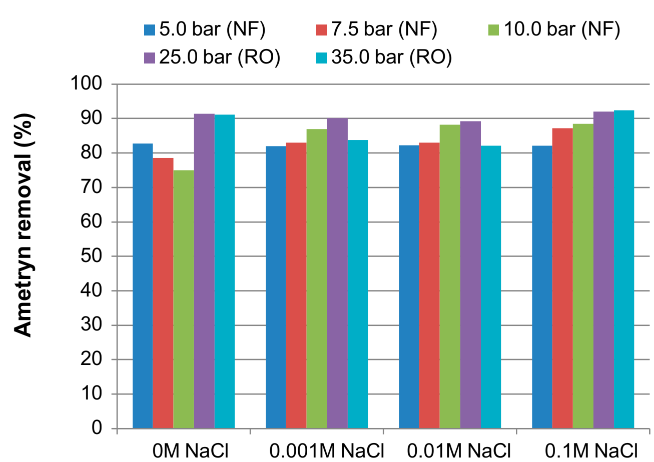


Fig. 4. Removal of ametryn for various pressures and ionic strengths.

Table 3
Summary of results for NF and RO (applied pressures varied from 5 to 10 bars in NF and 25 to 35 bars in RO)

	Ionic strength (M)							
	0.000		0.001		0.010		0.100	
	NF	RO	NF	RO	NF	RO	NF	RO
Adsorption (%)	15.39	0.98	2.82	9.65	0.00	0.00	0.71	0.00
Average removal (%)	78.76	91.31	84.03	86.94	84.47	85.71	85.91	92.21
Average flux ($L/m^2 h$)	64.28	55.56	66.41	58.12	65.61	34.03	55.14	32.52

clear trends at lower (NF) and higher (RO) applied pressure, in this study, ametryn did not show a clear trend at higher applied pressure. At lower applied pressure (NF), adsorption of ametryn (this study) and diuron [9] decreased with the increase in the concentration of NaCl; at higher applied pressure (RO), adsorption of diuron slightly increased with the increase in the concentration of NaCl and reached a stable value.

4.2. Removal of ametryn by NF and RO

The removal of ametryn is determined by analysing the permeate that was removed after the 6 h of adsorption. The values in Table 3 represent the average removal from a number of samples taken for each experiment.

As anticipated, the results show an increase in removal as ionic conditions are strengthened. This is clearly evident in Fig. 4 with an improvement in compound removal as the concentration of sodium chloride is increased.

The results of the individual experiments show that ionic conditions have little impact on rejection at low pressures through the NF membrane. However, as the pressure increased, the removal capabilities of the NF membrane improved as the ionic conditions were strengthened. Increase in the concentration of NaCl increases the adsorption of Na^+ onto membrane surface and reduces the pore size of the membrane which helps to increase the removal of ametryn. Similar results were obtained when diuron was used as the model solute [9]. The results of the RO experiments indicate that high ionic conditions provide the best outcome for ametryn removal. Having no ionic concentration was found to be more effective in removing ametryn across an RO membrane than have low to medium ionic conditions. Most of the results show that an increase in overall compound removal is achieved as the pressure is increased. This is shown by both the RO and NF membranes.

4.3. Flux obtained from NF and RO experiments

Table 3 shows adsorption and the removal of ametryn as well as flux during NF and RO at different ionic strengths. The results of the flux measurements are consistent with the predictions of the literature [9]. As Fig. 5 shows, the flux is generally higher through the NF membrane than through the RO membrane. Within each membrane, an increase in pressure generally results in an increase in flux. As expected, the flux decreased as the ionic conditions in the water increased. Increase in flux is associated with the decrease in removal and vice versa. Thus, the explanation given in section 4.2 can be used to describe the changes in flux in NF and RO when treating ametryn.

Table 3 summarises the adsorption and removal values and the recorded flux for each membrane under various ionic conditions. The most effective method of removal was to use RO with a NaCl concentration of 0.1 M.

4.4. Modelling the membrane pore size using the experimental flux and ametryn removal

A study by Chen et al. [11] explored the influence of molecular weight, molecular size and flux on

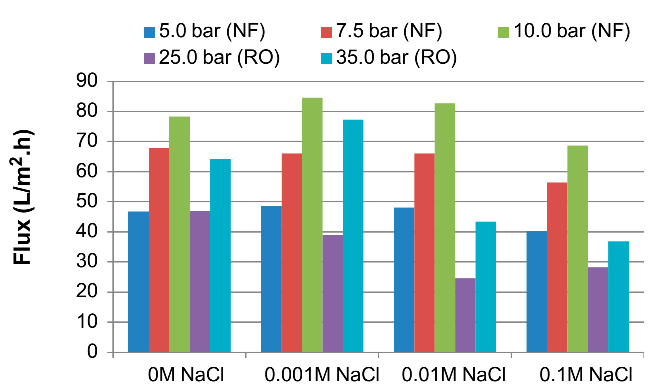


Fig. 5. Average flux values for various pressures and ionic strengths.

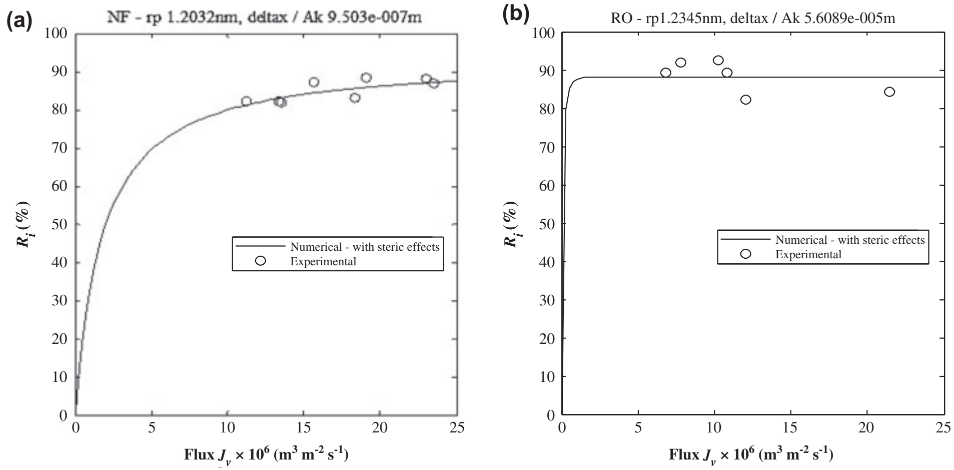


Fig. 6. Rejection models to determine theoretical pore sizes (molecular length and width of ametryn are 12.5 and 6.1 Å respectively). (a) NF membrane filtering ametryn (b) RO membrane filtering ametryn.

pesticide removal in nanofiltration membrane. The study found that an increase in molecular weight would lead to increased in pesticide rejection through the NF filter. It was found that atrazine had a rejection of between 86 and 95% through the membrane and diuron had a rejection rate of between 50 and 85% depending on the conditions. The study also found that molecular length was more influential on rejection than molecular width. Based on the experimental results, the rejection model was applied to both membranes in order to determine the theoretical pore sizes of each membrane (see Fig. 6(a) and (b)). From the modelling, both membranes were found to have an approximate pore size of 1.2 nm.

5. Conclusion

Performance of NF and RO in removing ametryn was evaluated in this study. When the ionic strength of a synthetic solution containing 1 mg/L of ametryn was increased from 0 to 0.1 M NaCl, adsorption and rejection of ametryn by NF and RO membranes were found to decrease and increase, respectively. Maximum adsorptions by NF and RO were 15.4 and 9.7%, respectively. Higher ionic strengths tend to shield the membranes and preventing them adsorbing ametryn. Similarly, the maximum rejections by NF (5–10 bar) and RO (25–35 bar) were 85.9 and 92.2%, respectively. Largest fluxes for NF and RO were found to obtain at 0.001 M ionic strength, and the values were 66.4 and 58.1 L/m^{2}h, respectively. Higher ionic strength increases the retention of NaCl that leads to the reduction in the pore size. This in turn increases the rejection of ametryn at higher ionic strengths.

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